

Electronic structure of KNbO_3 : $\text{Nb } M_{4,5}$ X-ray fluorescence measurements

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Mixed oxides of perovskite-type structure, depending on their composition, give rise to a variety of electric, magnetic and optical effects. Among these perovskite oxides, potassium niobate provides multiple electro-optical and catalytic applications [1], making the study of its electronic structure very important. Besides the typically used X-ray photoelectron spectroscopy (XPS), the X-ray emission spectroscopy (XES), which is an element- and partial state-sensitive technique, provides important experimental information about the spatial- and energy-resolved distribution of electronic states in the compound. For the study of dielectric materials, XES has certain advantages over XPS because it is not affected by charging effects, and the quality of the surface preparation is not so crucial. The measurements of the X-ray fluorescence while scanning the excitation energies below and beyond the excitation threshold of particular core states, which are possible at the ALS Beamline 8.0, open new opportunities for the study of soft x-ray resonant inelastic spectra (XRIS). It has been shown that these spectra may reveal some momentum-resolved information regarding the valence band dispersion [2-5].

We measured the $\text{Nb } M_{4,5}$ emission spectra in KNbO_3 over the range of excitation energies 206.5 to 240.6 eV. The interpretation of our data has been done based on first-principles calculations of the electronic structure, emission and absorption spectra by the all-electron full-potential linearised augmented plane-wave method.

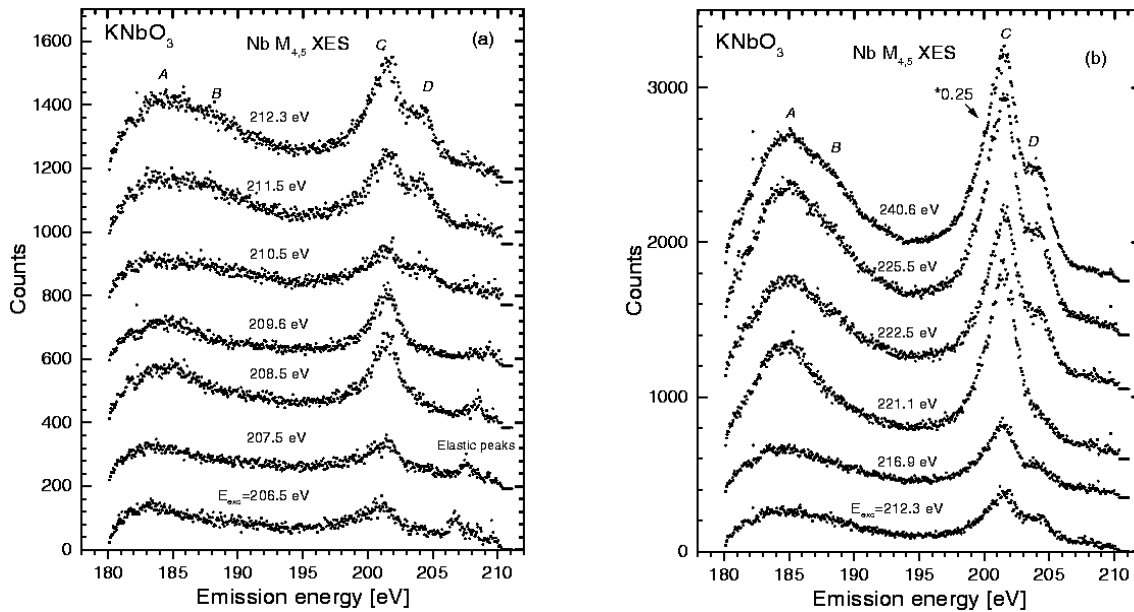


Figure 1. $\text{Nb } M_{4,5}$ emission spectra of KNbO_3 . The excitation energy is tuned through the Nb 3d-threshold from 206.5 to 212.3 eV (a) and from 212.3 to 240.6 eV (b).

In Fig. 1 (a-b) the Nb $M_{4,5}$ emission spectra of KNbO₃ are shown for various excitation energies near the Nb 3d threshold. Four features are observed and labeled A through D. The most dramatic changes in the shape of the fine structure of Nb $M_{4,5}$ emission spectra are found for excitation energies between 206.5 and 212.3 eV where new features (D and B) appear with changes in excitation energy. It is suggested in Ref. [6] that in Nb, $M_{4,5}$ emission reveals only the M_5 ($3d_{5/2}$) emission features because the M_4 ($3d_{3/2}$) is filled by radiationless transition. Therefore it was unexpected when we found the excitation energy dependence of Nb $M_{4,5}$ to be distorted by the spin-orbit splitting of the Nb 3d-levels and not revealing the band dispersion.

Fig. 2 displays a full calculation of the Nb $M_{4,5}$ emission spectra based on the Nb 5p and Nb 4f DOS modulated by the transition probabilities. In the calculation, the resulting spectrum has been simulated by shifting the two identical contributions by the value of the spin-orbit splitting in the Nb 3d shell, which amounted, according to our full-electron calculation, to 2.88 eV. These two contributions, corresponding to individual M_4 and M_5 spectra, were then summed up with relative weights of 2:3. It is found that the contribution of the Nb 4f states to the emission is negligible and only $5p \rightarrow 3d$ transitions are important for the interpretation of Nb $M_{4,5}$ XES. The O 2s states contribute to the Nb M_5 XES due to the O 2s - Nb 5p hybridization. The corresponding features in the Nb M_4 and M_5 XES near -16 eV and -13 eV are broadened in the experimental spectra but still recognizable in Fig. 1 as peaks A and B.

Going back to the discussion of the energy dependence of the Nb $M_{4,5}$ emission spectra in KNbO₃ (Fig. 1), we note that according to our XPS measurements the Nb M_5 ($3d_{5/2}$) and Nb M_4 ($3d_{3/2}$) binding energies are 207.2 and 210 eV, respectively (relative to the vacuum level). Conclusively the emission features in the spectra excited between 206.5 and 209.6 eV are generated by the refill of the Nb M_5 ($3d_{5/2}$) hole as excitation of Nb M_4 is not possible below 210 eV. In the excitation energy range between 210.5 and 216.9 eV additional features B and D appear as a result of contributing transitions to Nb M_4 ($3d_{3/2}$). The sharp increase in intensity in the emission spectra at excitation energies from 216.9 eV to 221.1 eV can be attributed to the threshold of the $3d \rightarrow 5p$ absorption. This is illustrated by the calculated Nb M_4 -absorption spectrum in Fig. 3. The $3d \rightarrow 5p$ absorption starts to contribute at an excitation energy of about 218 eV. The onset for the $3d \rightarrow 4f$ absorption occurs around 235 eV. The strong enhancements of the emission (see Fig. 1) occur when the excitation energy exceeds the M_5 threshold ($E_{\text{exc}}=208.5$ eV), M_4 threshold ($E_{\text{exc}}=211.5$ eV), the $3d \rightarrow 5p$ threshold ($E_{\text{exc}}=221.1$ eV) and the $3d \rightarrow 4f$ threshold ($E_{\text{exc}}=240.6$ eV) as displayed in the absorption spectrum (Fig. 3). We note that the spectrum excited at the $3d \rightarrow 4f$ threshold ($E_{\text{exc}}=240.6$ eV) is divided by 4 in order to display all spectra on the same scale.

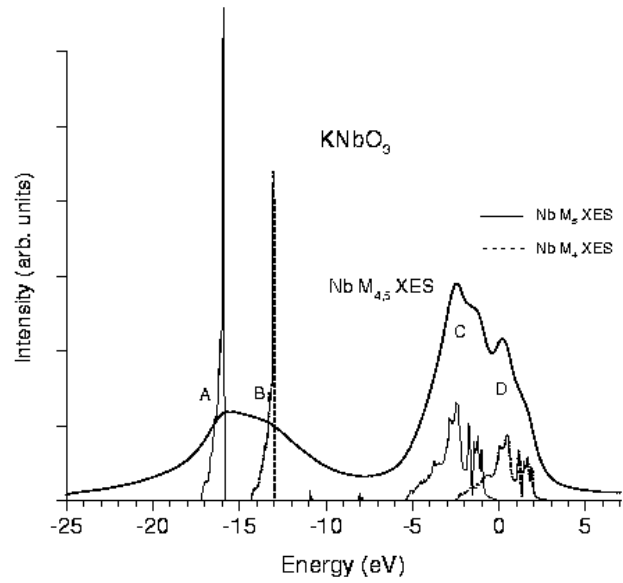


Figure 2. Calculated Nb $M_{4,5}$ XES of KNbO₃ broadened for instrumental distortion (0.2 eV), core level life-time (0.35 eV) and valence life-time (2.0 eV). The contributions of unbroadened M_5 and M_4 spectra are also shown.

The emission spectrum corresponding to the excitation energy of 221.1 eV in Fig.1 exhibits, as compared with that for $E_{\text{exc}} = 216.9$ eV, strongly enhanced M_5 but relatively unchanged M_4 intensity. Therefore, this specific selective excitation of Nb M_5 XES can be also used to receive experimental information about the Nb $5p$ DOS undistorted by overlapping with Nb M_4 XES. Starting from $E_{\text{exc}} = 222.5$ eV, the resonant emission gets enhanced for the M_4 component as well, so that the original shape of the spectrum (for smaller excitation energies) is roughly restored, but with much higher intensity.

To summarize, we have measured soft x-ray emission spectra excited through the Nb $3d$ threshold. The spectra show dispersion and are explained by the calculations (based on DOS and full band structure calculations). The changes in the spectra occur at the $3d_{5/2}$, $3d_{3/2}$, $3d-5p$ and $3d-4f$ thresholds of the absorption. Tuning the excitation energy to the corresponding thresholds of the absorption spectrum allows us to attribute contributions from the decay of the $3d_{5/2}$ holes (peaks C and A) and the $3d_{3/2}$ holes (peaks D and B) via valence emission. The overlap of these two spectra complicates the analysis of the excitation energy dependent trends in the resonant emission which otherwise would be able to provide key information about band dispersion, as shown by studies of other materials [2, 3].

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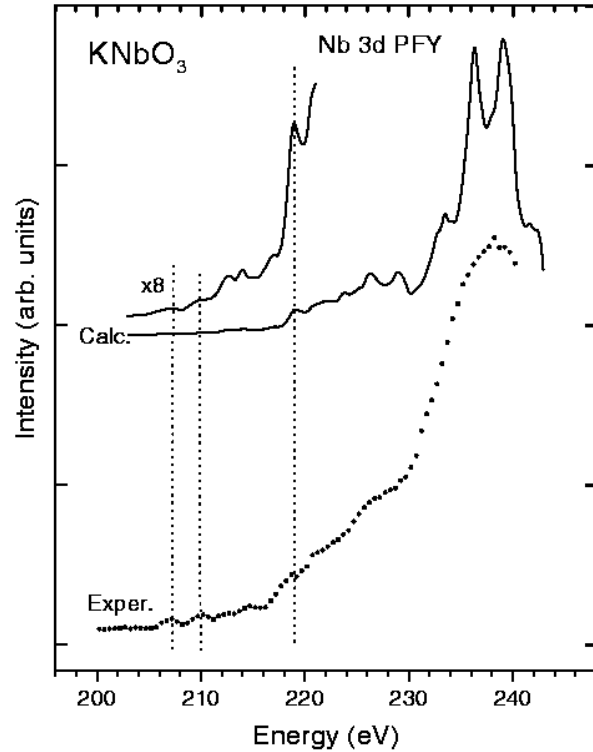


Figure 3. Calculated and measured partial fluorescence yield at the Nb $3d$ threshold.